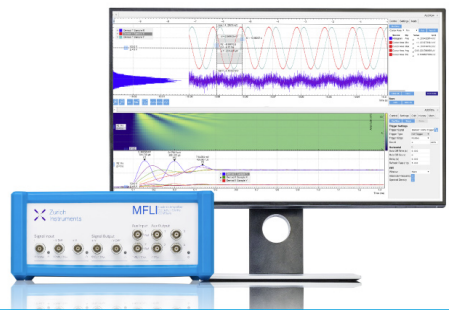
The Journal of Chemical Physics

Response to "Comment on 'On the development of polarizable and Lennard-Jones force fields to study hydration structure and dynamics of actinide(III) ions based on effective ionic radii'" [J. Chem. Phys. 150, 097101 (2019)]

Cite as: J. Chem. Phys. **150**, 097102 (2019); https://doi.org/10.1063/1.5087193
Submitted: 29 December 2018 . Accepted: 13 February 2019 . Published Online: 07 March 2019

Riccardo Spezia, Valentina Migliorati, and Paola D'Angelo



The Journal of Chemical Physics RESPONSE scitation.org/journal/jcp

Response to "Comment on 'On the development of polarizable and Lennard-Jones force fields to study hydration structure and dynamics of actinide(III) ions based on effective ionic radii'" [J. Chem. Phys. 150, 097101 (2019)]

Cite as: J. Chem. Phys. 150, 097102 (2019); doi: 10.1063/1.5087193
Submitted: 29 December 2018 • Accepted: 13 February 2019 •
Published Online: 7 March 2019

Riccardo Spezia,[1,a)] Valentina Migliorati,[2] and Paola D'Angelo[2]

AFFILIATIONS

[1] LAMBE, Université d'Evry Val d'Essonne, CEA, CNRS, Université Paris Saclay, F-91025 Evry, France
[2] Dipartimento di Chimica, Università di Roma "La Sapienza", Roma, Italy

[a)] **Electronic mail:** riccardo.spezia@sorbonne-universite.fr. **Present address:** Laboratoire de Chimie Theorique, Sorbonne Université and CNRS, F-75005 Paris, France.

https://doi.org/10.1063/1.5087193

In the comment[1] on our previous paper,[2] Lundberg and Persson are concerned with the behavior of metal ion-oxygen (M–O) distances along the actinoid(III) ion (An(III)) series in an aqueous solution as they disagree with X-ray determinations on hydrated crystals. Our article reports molecular dynamics (MD) simulations using polarizable and non-polarizable force fields, and it is focused on structural and dynamical differences obtained comparing the two methods. Extended X-ray absorption fine structure (EXAFS) data are used to better evaluate the simulation results. One important point of their criticism is on the EXAFS data to which our simulation results are carefully compared (finding a good agreement) as they have recently discussed in a review paper.[3] In particular, their criticism is focused on the ability of the EXAFS spectroscopy to carefully determine the structural properties of solvated clusters. Here, we better clarify some points focusing in particular on the results reported for structures with a coordination number (CN) of 9 having a tricapped trigonal prism (TTP) structure.

In their comment,[1] Lundberg and Persson compare X-ray diffraction distances of crystals with the ones estimated by EXAFS and simulations in liquid phase claiming the existence of important differences that would suggest a misinterpretation. We should note that the difference between the crystallographic and the EXAFS determination is almost negligible for U(III) and it (slightly) increases across the series: for Cf(III), the difference in Cf–O distance is 0.043 and 0.015 Å with respect to EXAFS and polarizable MD data, respectively. Distances obtained for CN = 9 are summarized in Table I. From simulations, we estimated an uncertainty of 0.02 Å so differences with respect to X-ray diffraction data are inside this value. For EXAFS, we can estimate an uncertainty on distances of about 0.01 Å. X-ray diffraction determinations are of course very precise, but in the present case, one should consider two aspects: (i) experiments are carried out on different crystal systems, while Lundberg and Persson assumed that they behave as aqua ions in liquid water and (ii) only for U(III), Pu(III), and Cm(III), there is more than one crystallographic structure reported in the literature. Notably, Lundberg and Persson reported two values for U(III), three for Pu(III), and two for Cm(III) (see Table I). For U(III) and Cm(III), there is a variability on the crystallographic distances of 0.016 and 0.006 Å, which is an indication that reasonable fluctuations should be in the 0.01-0.02 Å range. Furthermore, temperatures are also variable among different crystals, ranging from 100 to 293 K as carefully reported by Apostolidis *et al.*[4] To better evaluate distance fluctuations that can be obtained by comparing different crystallographic structures, data reported by Lundberg and

TABLE I. An–O distances (in Å) for CN = 9 as reported by different theoretical and experimental studies.

An(III)	Pol-MD[a]	EXAFS single shell[5]	EXAFS two-shell[5]	X-ray Lundberg and Persson[3]	X-ray original data	Other MD	EXAFS other data
U	2.53 (2.50)	2.527	2.50; 2.58	2.521; 2.537	2.509; 2.595[4]		2.52[6]
Np	2.51 (2.48)	2.509	2.48; 2.56	2.517	2.490; 2.571[4]		2.50[6]
Pu	2.50 (2.47)	2.490	2.45; 2.55	2.505; 2.507	2.472; 2.571[4]	2.56[b]	2.51[6]
				2.508	2.476; 2.574[7]		
Am	2.49 (2.45)	2.472	2.43; 2.54	2.503	2.466; 2.578[8]	2.53[c]	
Cm	2.47 (2.43)	2.455	2.40; 2.53	2.490; 2.484	2.454; 2.565[8]	2.48[d]; 2.55[e]	2.47[9]
					2.453; 2.545[9]	2.52[f]	
Cf	2.45 (2.41)	2.422	2.37; 2.49	2.465	2.422; 2.550[4]	2.54[g]	2.42[10,11]

[a]MD simulations from polarizable force field from Ref. 2 (see Table II of the same reference for more details and results of Lennard-Jones). We report average values (for which an uncertainty of ±0.02 Å was estimated) and maximum of An–O radial distribution function (in parentheses).
[b]DFT-based MD simulations[12] with CN = 9. Note that the authors report CN = 8 as more stable with Pu–O = 2.53 Å.
[c]MD of Pérez-Conesa *et al.*[13] They obtained Am–O = 2.47 Å for CN = 8.
[d]DFT-based MD.[14]
[e]Polarizable MD[15] with CN = 8.9.
[f]Non polarizable MD.[14]
[g]MD simulations[16] with CN = 8.6. The authors report shorter distances (2.43–2.48 Å) for lower CNs.

Persson for lanthanoid(III) (Ln) ions provide some information.[3] By considering only structures with CN = 9, we may estimate an uncertainty in the 0.03–0.05 Å range. All these considerations should bring to the conclusion that the uncertainty associated with An–O distances in liquid water is smaller (or equivalent) than that of different X-ray structures, and discussions on the discrepancy between crystal and liquid structures must take into account this aspect in a more critical way.

Other experiments and calculations have been carried out in the past, and we have listed An–O distances for aqua ions with CN = 9 in Table I for completeness. In particular, it can be noticed that if one compares the two-shell EXAFS fits with the detailed X-ray diffraction data, where prismatic and capped An–O distances are reported separately, it appears that across the series, the differences between EXAFS and X-ray values are not sensibly large. Note that other simulations reported in the literature found An–O distances longer than X-ray ones, as summarized in Table I. Studies reporting CN = 8 are also present, and they cannot be totally disregarded (see our previous review[17]). Another point that should be considered when comparing with crystal structures is the breaking of symmetry. The maximum of the An–O radial distribution function as obtained by polarizable MD simulations gives a measure of the asymmetry: if one considers a purely symmetric An–O distribution function (and thus an underlying harmonic motion), the maximum and the average distance should coincide. As one can notice, there is a difference of 0.03–0.04 Å which also should be considered when comparing with crystal structures.

Lundberg and Persson say that "the EXAFS technique severely underestimates the contribution at larger distances," but this is only true at the end of the An(III) series, while the U(III)–O distance determined by EXAFS is equal to X-ray values. Note that the correct determination, according to the comment,[1] is obtained for the ion that coordinates at larger distances, the U(III). In the case of Cf(III), the ion-oxygen distances are shorter, while the difference between the EXAFS and X-ray diffraction determinations is larger. This is clearly an unexplained contradiction. EXAFS sensitivity cannot change in going from U(III) to Cf(III). The small difference in An–O distances has to be ascribed to the different behavior of a crystalline species as compared to an ion dissolved in water. The difference becomes larger at the end of the series as the water exchange rate increases along the series. For Cf(III), the water dynamics is more important and also CN = 8 contributes in determining the final average distance, as detailed in our simulations[2] and also by previous EXAFS and Monte Carlo simulation studies.[11]

Recently, the Ac(III) ion in liquid water has been studied experimentally.[18–20] Ac–O distances are reported in the 2.59–2.68 Å range with CN estimated in the 9–11 range. Lundberg and Persson have thus extrapolated from crystal data an Ac–O distance of 2.56 Å which was compared with the value reported[18] for the aqua ion of 2.63(1) Å with CN = 10.9 ± 0.5. They say that "the expected Ac–O bond distance would be 2.560 Å meaning that the higher coordination number given is correct." We have extrapolated Ac–O distance using EXAFS (single shell) and polarizable MD results, obtaining 2.59 and 2.64 Å, respectively. Note that Ferrier *et al.*[18] reported a density functional theory (DFT)-based MD simulation where an Ac–O distance of 2.689 ± 0.11 Å was found with CN = 9. An independent simulation study[21] provided a distance of 2.65 Å with CN = 9. These results show that a CN = 9 is possible even for larger distances. Surely, for Ac(III) hydration, more experimental and theoretical studies are needed to better elucidate its structure and to have more data on the actinoid(III) series.

One important feature of ions in water is solvent dynamics which has an impact in resulting structures and observables. This was largely studied for Ln(III) ions,[22,23] and the picture seems to be similar for An(III).[2,24] Both inter- and intra-shell exchange dynamics play a role in first shell structural

characterization. First shell water self-exchange was studied experimentally for Ln(III) ions with rate constant values in the 0.2-1.19 ns^{-1} range for the beginning of the series (where CN = 9 is dominant).[25,26] For An(III), unfortunately there are no experimental data, but simulations found results similar to Ln(III) series (see Table IV of our paper[2]). This dynamic behavior is at the basis of a not-negligible asymmetry which must be considered in the EXAFS data analysis in liquid and which is less present in crystals. The second important aspect is the intra-shell exchange. The identified TTP structure in liquid should not be seen as a static structure like in a crystal: there is a continuous interchange between prismatic and capped positions of the same water molecule. A detailed study was reported for Ln(III) aqua ions.[27] These two contributions of water dynamics are at the basis of the EXAFS fitting which is carried out starting from the radial distribution functions. In this way, it is possible to directly account for the position configurational average[28–32] in the calculation of the $\chi(k)$ signal instead of calculating several EXAFS signals associated with different configurations and making an average of the $\chi(k)$ signals *a posteriori*.

Finally, diffusion coefficients[33] and hydration energies[34,35] are also available for An(III) in water. Polarizable MD simulations have correctly reproduced these data[36] and in particular the non-trivial behavior of diffusion coefficients, which is related to the situation of highly charged and small ions in a solvent with high dielectric constant.[37] This provides an additional source, independent of EXAFS measurements, to strengthen the hydration picture resulting from MD simulations.

REFERENCES

[1] D. Lundberg and I. Persson, J. Chem. Phys. **150**, 097101 (2019).
[2] R. Spezia, V. Migliorati, and P. D'Angelo, J. Chem. Phys. **147**, 161707 (2017).
[3] D. Lundberg and I. Persson, Coord. Chem. Rev. **318**, 131 (2016).
[4] C. Apostolidis, B. Schimmelpfennig, N. Magnani, P. Lindqvist-Reis, O. Walter, R. Sykora, A. Morgenstern, E. Colineau, R. Caciuffo, R. Klenze, R. Haire, J. Rebizant, F. Bruchertseifer, and T. Fanghänel, Angew. Chem., Int. Ed. **49**, 6343 (2010).
[5] P. D'Angelo, F. Martelli, R. Spezia, A. Filipponi, and M. A. Denecke, Inorg. Chem. **52**, 10318 (2013).
[6] B. Brendebach, N. L. Banik, C. M. Marquardt, J. Rothe, M. Denecke, and H. Geckeis, Radiochim. Acta **97**, 701 (2009).
[7] J. Matonic, B. Scott, and M. Neu, Inorg. Chem. **40**, 2638 (2001).
[8] P. Lindqvist-Reis, C. Apostolidis, J. Rebizant, A. Morgenstern, R. Klenze, O. Walter, T. Fanghänel, and R. G. Haire, Angew. Chem., Int. Ed. **46**, 919 (2007).
[9] S. Skanthakumar, M. Antonio, R. Wilson, and L. Soderholm, Inorg. Chem. **46**, 3285 (2007).
[10] R. Revel, C. Auwer, C. Madic, F. David, B. Fourest, S. Hubert, J. Du, and L. R. Morss, Inorg. Chem. **38**, 4139 (1999).
[11] E. Galbis, J. Hernandez-Cobos, C. D. Auwer, C. L. Naour, D. Guillaumont, E. Simoni, R. R. Pappalardo, and E. Sanchez-Marcos, Angew. Chem., Int. Ed. **49**, 3811 (2010).
[12] S. O. Odoh, E. J. Bylaska, and W. A. de Jong, J. Phys. Chem. A **117**, 12256 (2013).
[13] S. Pérez-Conesa, J. M. Martínez, R. R. Pappalardo, and E. Sanchez Marcos, Inorg. Chem. **57**, 8089 (2018).
[14] R. Atta-Fynn, E. J. Bylaska, G. K. Schenter, and W. A. de Jong, J. Phys. Chem. A **115**, 4665 (2011).
[15] D. Hagberg, E. Bednarz, N. M. Edelstein, and L. Gagliardi, J. Am. Chem. Soc. **129**, 14136 (2007).
[16] E. Galbis, J. Hernandez-Cobos, R. R. Pappalardo, and E. Sanchez-Marcos, J. Chem. Phys. **140**, 214104 (2014).
[17] P. D'Angelo and R. Spezia, Chem. - Eur. J. **18**, 11162 (2012).
[18] M. Ferrier, B. Stein, E. Batista, J. Berg, E. Birnbaum, J. Engle, K. John, S. Kozimor, J. Lezama Pacheco, and L. Redman, ACS Cent. Sci. **3**, 176 (2017).
[19] M. Ferrier, B. Stein, S. Bone, S. Cary, A. Ditter, S. Kozimor, J. Lezama Pacheco, V. Mocko, and L. Redman, Chem. Sci. **9**, 7078 (2018).
[20] M. Ferrier, E. Batista, J. Berg, E. Birnbaum, J. Cross, J. Engle, H. La Pierre, S. Kozimor, J. Lezama Pacheco, B. Stein, S. Stieber, and J. Wilson, Nat. Commun. **7**, 12312 (2016).
[21] N. Morales, E. Galbis, J. M. Martinez, R. R. Pappalardo, and E. Sanchez-Marcos, J. Phys. Chem. Lett. **7**, 4275 (2016).
[22] M. Duvail, R. Spezia, and P. Vitorge, ChemPhysChem **9**, 693 (2008).
[23] M. Duvail, P. Vitorge, and R. Spezia, J. Chem. Phys. **130**, 104501 (2009).
[24] M. Duvail, F. Martelli, P. Vitorge, and R. Spezia, J. Chem. Phys. **135**, 044503 (2011).
[25] L. Helm and A. E. Merbach, J. Chem. Soc., Dalton Trans. **2002**, 633.
[26] L. Helm and A. E. Merbach, Chem. Rev. **105**, 1923 (2005).
[27] F. Sessa, R. Spezia, and P. D'Angelo, J. Chem. Phys. **144**, 204505 (2016).
[28] V. Pham, I. Tavernelli, C. Milne, R. van der Veen, P. D'Angelo, C. Bressler, and M. Chergui, Chem. Phys. **371**, 24 (2010).
[29] P. D'Angelo, A. Di Nola, A. Filipponi, N. V. Pavel, and D. Roccatano, J. Chem. Phys. **100**, 985 (1994).
[30] V. Migliorati, G. Chillemi, and P. D'Angelo, Inorg. Chem. **50**, 8509 (2011).
[31] P. D'Angelo, A. D. Nola, M. Mangoni, and N. V. Pavel, J. Chem. Phys. **104**, 1779 (1996).
[32] P. D'Angelo, A. Lapi, V. Migliorati, A. Arcovito, M. Benfatto, O. M. Roscioni, W. Meyer-Klaucke, and S. Della-Longa, Inorg. Chem. **47**, 9905 (2008).
[33] B. Fourest, J. Duplessis, and F. David, Radiochim. Acta **36**, 191 (1984).
[34] Y. Marcus, Biophys. Chem. **51**, 111 (1994).
[35] F. David and V. Vokhmin, New J. Chem. **27**, 1627 (2003).
[36] F. Martelli, S. Abadie, J.-P. Simonin, R. Vuilleumier, and R. Spezia, Pure Appl. Chem. **85**, 237 (2013).
[37] F. Martelli, R. Vuilleumier, J.-P. Simonin, and R. Spezia, J. Chem. Phys. **137**, 164501 (2012).